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A Management Study on Recovery and Recycling of Useful Material in Leather Tanning Industry

***Moghira Badar*[*], *Imran Ali*[**] *and Muhammad Luqman*[***]**
[*]*Department of Environmental Management,*
National College of Business Administration and Economics, Lahore, PAKISTAN
[**]*Hailey College of Commerce, University of the Punjab, Lahore, PAKISTAN*
[***]*Department of Management Sciences, University of Sargodha, Lahore campus, PAKISTAN*

(Corresponding author: Moghira Badar, moghirab@yahoo.com)
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ABSTRACT: This paper deals with the process development for recycling of waste chemicals. Basic chromium sulfate (BCS) is one of the expensive and widely used chemicals in chrome tanning process. We have economically recovered BCS up to 99 % however 1% is left as impurity in effluents. Sodium sulphide is recovered up to 99.5 from the composite wastewater using the very economical method. This paper also deals with the locally devolved technique of de-liming by the use of CO_2. The results show that in case of skins, the use of ammonium sulfate can be completely eliminated where as in case of bovine hides the use of ammonium sulfate can be reduced to 20 to 50% (w/w), depending upon the thickness of the pelt (limed hides or skins). These results in proportional reduction of ammonia gas produced along with the reduction in concentration of BOD, COD and sulfate ions by the same amount.

Key words: Liming process, Chromium Recovery, Precipitation Agent, Float, Chromium Sulphate

INTRODUCTION

Tanning industry uses a number of chemicals during the process, only a part of a chemical is consumed and the rest ends up in the effluent as pollutant. As per our cleanser production options, the chrome recovery, lime recycling and reuse of pickle float have been found out most important in chemical and water conservation and reduces significant environmental pollution lad form the tanning industry (Fatima et al., 2016).

Additionally, the system can also produce hot water while cooling the boiler off gases from 280-220 ^{o}C to 105 ^{o}C the quantity of hot water generated depends upon the quantity of boiler off gases being cooled. Calcium Hydroxide has been recovered up to 68% from leather tannery unhairing wastes by processes, which may be adoptable to commercial use. It is also an estimated the cost analysis of total and individual recycling of different Chemicals used in different tanning process.

This study has been conducted as a part of the research project for the tanneries of the Punjab. Feats of three processes causing 65 to 75% of the total effluent pollution were selected for recycling the chemicals from the chrome tanning process, liming process and pickling process (Badar *et al.,* 2016)**.**

To study the above-mentioned options, full-scale recycling systems were installed in one tannery (Star Leather Industries) under the Pollution control project. Tannery staff was helped to monitor the processes and analyses were conducted in the in-house laboratory mainly. Ten drums were used during this study, and weight processed in each drum was 3,000 kg. All three selected processes were recycled for 10 continuous days. Necessary environmental parameters were monitored at the process level and at the final effluent drain, after the primary wastewater treatment plant, both with recycling options for 10 days and for 3 days without recycling at the end. Concentration of unexhausted chemicals in all these recycling options were also analyzed to quantify the amount of fresh chemicals needed to be added in the spent liquor to recycle for the next batch and for the study of financial aspects and payback period (Badar *et al.,* 2016).

These are the objectives of this study are that to determine efficiency of different recycling options: and financial and environmental impacts of selected recycling options, including quality of leather.

MATERIALS AND METHODS

A. Chemical and float

Chemicals and water used in the processes were taken based on the pelt weight of hide. The float taken for tanning and pickle process was 80% and 175% of pelt weight in liming process. The range of chemicals, %age of pelt weight used, and their concentration in float are as given in Table 1.

Table 1: Chemical concentration in floats.

Sr. No.	Process	Name of Chemical	Chemical (%) of pelt weight	Concentration in floats g/l
	Chromium tanning	Chromium Sulphate	5.0	62.5
	Pickle	1. Sulphuric acid	2.0	25.0
		2.Sodium chloride	8.0	100.0
		3.Sodium formate	1.5	18.7
	Liming	1. Sodium sulphate	4.0	22.8
		2.Calcium hydroxide	4.0	22.8

B. Recycling techniques

The recycling techniques or cleaner options studied are as listed below:

Chrome tanning float: After tanning process the spent float from each drum was pumped in a fiberglass tank and pH was adjusted from 3.8 to 2.8 using sulfuric acid. After Cr_2O_3 analyses, the spent float was recycled for the next lot coming after pickling process. The fresh powder $Cr_2(SO_4)_3$ used was 70% only and 30% was taken from the recycled float.

Liming float: Similar to above recycling technique, the spent float from the liming process was collected in the fiberglass tank and analyzed for hydrated lime and sodium sulfide. Spent liming float was recycled back for the next batch and completed the process by adding the required quantity of sodium sulfide and lime (Moghira *et al.,* 2016).

Picking float: After pickling process, the spent float was pumped in the fiberglass tank and analyzed for sulfuric acid, sodium chloride and sodium formate. Spent pickle float was recycling back for the next batch before tanning (Kim DS *et al.,* 1995). The required exhausted chemicals were added to meet the require recipe.

RESULTS AND DISCUSSION

A. Chrome recycling

Chromium metal in the trivalent form is used for leather tanning in the world over. Commercially it is available in the form, basic chromium sulfate (BCS), containing about 26% chromium oxide of 33% basicity. During tanning about 5-7% of pelt weight, BCS is applied. It imparts higher shrinkage temperature, softness, fullness and preservation to the leather. Approximately 63% (135) of 216 tanneries of Punjab are using BCS in tanning and re-chroming process to produce leather of different properties and qualities. The estimated chromium sulfate consumption in these tanneries is 27,657 kg/d. about 7,740 (28%) kg/d BCS is being wasted (survey report 1999 by ICTP) (Peters TB *et al.,* 2010).

Such huge quantity of this precious chemical is not only an economic loss to the tanners of Punjab but also poses significant environmental impacts on the water bodies (Daniel RC *et al.,* 2011).

Table 2: Chrome concentration in spent liquor.

Cycle No	BCS in spent liquor (g/l)	BCS Wasted (%)
1	14.06	23.36
2	14.04	23.04
3	15.02	24.32
4	15.04	24.64
5	15.06	24.96
6	15.04	24.64
7	15.06	24.96
8	14.04	23.04
9	15.04	24.64
10	14.02	22.72
Average	15.02	24.03

By chrome recycling system the spent chrome can be recycled back for tanning processes, without compromising any leather quality, which is normally 20-30% of the BCS applied. The concentration of chrome in the spent liquor for 10 continuous days is as listed in Table 2. The discharge of BCS is in the range of 14.2 g/1 to 15.6 g/1. The BCS applied in each batch was 62.5g/1(5%). The difference in effluent concentration is due to small variation of float volume and the chrome exhaustion. The average chrome wastage in this particular tannery is 24%. By direct chrome recycling the saving is about Rs. 453,600 per annum at the production capacity 30,000 kg/d, where as the capital investment of chrome recycling system was about Rs. 650,000 (pay back period 1.5 month).

B. Lime recycling

Liming is a process for the removal of epidermal system and pigmentary matter from the hide .the epidermal system consists mainly of the protein keratin. A proper liming is necessary for smooth grained, non-cracky leather, processing a tight grain break and high tensile strength. The most commonly used method of depilation is the immersion of the stock in calcium hydroxide and sodium sulphate solution. The amount of lime and sodium sulphate added is about 4% of the pelt weight.

The concentration of Calcium Hydroxide and Sodium Sulfide in the spent liming liquor is as listed in table 4.

Table 3: Average concentration of pollutants.

Sr. No.	Parameter	Concentration (mg/l)	Pollution load(Kg/d)	% of total pollution load
1	BOD	1513	37	2
2	COD	4995	120	7
3	TSS	1603	38	2
4	TDS	33580	806	45
5	Sulphate	17498	420	24
6	Chloride	12160	292	16
7	Chromium	1258	61	4

Table 4: Concentration of Calcium Hydroxide and Sodium Sulfide in the spent liming liquor.

Cycle No.	Calcium Hydroxide (g/l)	Sodium Sulfide(g/l)
1	6.25	8.50
2	7.10	9.60
3	6.75	10.10
4	6.50	8.95
5	7.20	10.60
6	7.80	10.75
7	7.65	8.30
8	8.10	9.55
9	6.36	10.30
10	6.90	10.75
Average	7.06	9.71

Mean of 10 cycles reveal, 28% saving of Calcium Hydroxide and 39% saving in sodium sulfide. The cost saving is Rs. 37,632 and Rs. 196,560 per month out of lime and sodium sulfide respectively. The capital investment of lime recycling system is about Rs. 700,000 and payback period is less than three months.

The average concentration of different pollution parameters and their load during the 10 days monitoring is as shown in Table 5. The above table shows high % of BOD, COD and TDS pollution load. Comparatively low TSS values are due to sieving of spent liquor by the fine screens. The concentration of sulfide is 3,996 mg/1, whereas NEQS limit is only 1.0 mg/1 in the final effluent. By recycling of the lime spent liquor would ultimately lower the pollution load at the final drain significantly. Without lime recycling the high sulfide concentration requires very high investment for treatment (Reed S., 2010).

C. Pickle recycling

The objective of pickling is to completely remove the lime and acidify the stock in a solution of sodium chloride, sodium formate and sulfuric acid for about 4-6 hrs until a pH of 2.5 to 3.5 is achieved. This acidic pH before chrome tanning reduces the astringency of the chrome-tanning agents.

Table 5: Average concentration of different pollution parameters in liming spent liquor.

Sr. No.	Parameter	Concentration mg/l	Pollution load kg/d	% of total pollution load
1.	BOD	20111	1056	18.4
2.	COD	43693	2294	40
3.	TSS	10891	572	10
4.	TDS	30591	1660	28
5.	Sulphate	3969	210	3.6

In general after the completion of pickling, basic chromium sulfate is added in the same bath to start the chrome tanning process. So all the load is carried over to the tanning process. But to recycle the chrome-tanning float, one have to drain out the spent pickle float. Which contains high concentration of unexhausted chloride ions and sodium formate and sulfates. The recycling of pickle float would help reduce the pollution load and save the unexhausted chemicals also. The concentration of different chemicals present in the spent pickle float is as given in Table 6.

Table 6: The concentration of different chemicals present in the spent pickle float.

Cycle No.	Sodium chloride (g/l)	Sodium Formate (g/l)	Sulfuric acid (g/l)
1	40.30	8.00	8.00
2	29.24	9.50	8.33
3	40.30	9.25	7.84
4	41.75	8.75	7.84
5	41.54	8.50	8.50
6	40.70	8.50	8.33
7	41.13	9.00	7.68
8	41.37	8.25	7.35
9	41.60	9.25	8.00
10	39.50	9.75	8.00
Average	40.74	8.87	7.98

Table 7: Cost Analysis of effluent with and without recycling of Chemicals used in tanning process *1 Dollar = 104.70 Rs.

Parameters	Without Recycling		With Recycling		% Pollution Load Reduction with Recycling	Saving Pollution charges per Month *Rs.
	g/l	Kg/day	g/l	Kg/day		
Chromium	7	68.3	2	8.1	88	3009
Sulfide	74	136.6	8	12.1	91	6224
Sulfate	625	1275.6	20	350.9	73	46236
Chloride	640	2857.4	980	1336.1	53	76065
TSS	350	1059.8	75	253.1	76	40332
TDS	700	604.55	250	2867.9	53	158830
COD	750	2158.8	050	708.5	67	72512
BOD	85	616.2	10	209.2	66	20351
Total		14217.2		5745.9		423559

The quantity of sodium chloride saved for the next pickling process is 41%, sulfuric acid 28% and sodium formate was about 43%. Total chemical saving is about Rs. 216,000 per month, at Production capacity of 30,000 kg per day. Investment cost for the pickle recycling system is Rs. 500,000 and payback period is 2.5 months only. The average concentration of different pollution parameters and their load during the 10 days monitoring is as shown in Table 7.

D. Effluent Pollution Load

During the recycling period, 10 days and following 3 days, without recycling, the effluent at final drain was monitored regularly and composite sample were prepared and analyzed daily after the primary treatment plant. The average flow rat was about 674.8 m^3/d, during recycling period and 785m^3 /d without recycling. The comparison of pollution load of different pollution load of different pollution parameter with and without recycling is as given in Table 7.

Table 7 shows that all these recycling options are very much effective in pollution load reduction along with water conservation. The pollution load reduction of different parameters is in the range of 53 to 91%. Sulfide and chromium reduction is in the range of 88 to 91%. The chromium concentration in the effluent using recycling system is 12 mg/1 and sulfide is 18mg/1. This concentration is due to re-chroming, washing and fleshing (Russell RL *et al.*, 2009).

BOD load reduction is about 407 kg/d (66%), with recycling system. Other than chemical saving, it substantially reduces the capital investment of wastewater treatment plant and operation and maintenance cost also. The capital investment cost of wastewater treatment plant is bout Rs., 28,000/kg of BOD load, at this level of pollution load. With the recycling options the industrialist save Rs. 423,559 per month and Rs. 42,356 per month during the first year, based on 10% charge only (Dunn K., 2010).

Moreover the leather produced form all these recycling options passed all quality tests and rather trend of improvement in leather quality has been observed.

CONCLUSION AND RECOMMENDATIONS

It is concluded that here recycling of chrome lime and pickle are very much effective in reducing the pollution load at the final drain and are equally effective source of chemical land water conservation. All these options are financially feasible without any compromising leather quality.

Chrome recycling system results in, 24% basic chromium sulfate cost saving. Whereas with recycling, its concentration lowered down from 87 mg/1 to only 12mg/1 and chromium load reduction was about 60 kg/d. which is still higher than the NEQS limit of 1.0 mg/1 and needs further treatment of comply with this standard. Which is possible by separate treatment of chrome contaminated stream. Sulfate reduction is quite significant, which is about 925 kg /d (73%) and final effluent comply NEQS limit of 600mg/l.

It is recommended to adopt further cleaner production options like, slat dedusting, recycling of de-dusted salt in the pickle processes, CO_2 Deliming and dye recycling for chemical saving and further reduction of pollution load from the final drain.

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